THE EFFECT OF ALUMINUM ADDITIVE ON THE CUBIC EXPANSIVITY OF A COMPOSITE PLASTIC MATERIAL

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THESIS

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ON THE CUBIC EXPANSIVITY

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ABSTRACT

The need for a correlation between the amount of a substance added to a composite plastic material and its effect on the cubical coefficient of thermal expansion, or cubic expansivity, of the composite mixture is discussed. Experimental values for the cubic expansivities of several composite plastics made from a thermoplastic resin, an inert salt filler, and various percentages of aluminum are reported. Four hypothetical correlations are tested, two of which are reported to give calculated values within 1% of those observed. Apparatus and procedures for obtaining these results are also described in detail.

The writer wishes to express his appreciation for the assistance and encouragement given him in this investigation by Professor Richard A. Reinhardt of the U. S. Naval Postgraduate School and by Mrs. Mary M. Williams of the Research Department, U. S. Naval Ordnance Test Station, China Lake, California. The writer wishes to express his appreciation for the loving patience and assistance given him by his wife, Ann, throughout this investigation and in the preparation of this work.

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Symbols:

a	Cubical expansivity, cm^3/cm^3-°C
$a_{(mix)}$	Cubical expansivity of a mixture
b	An expansivity parameter of a mixture component dependent on its bulk compression modulus and its density
c	Linear expansivity, cm/cm-°C
n	Weight % of a component in a mixture
T	Temperature in degrees Centigrade, °C
V	Volume, cm^3
V_o	Initial volume of specimen bulb
ΔT	Temperature difference
ΔV	Net volume change which includes the combined expansions of mercury, sample and glassware

Subscripts:

X%	x weight percent of aluminum in the sample
g	glassware
m	mercury
s	sample

1. Introduction

In the plastics industry some years ago, great difficulty was obtained in attempting to cement a panel of an aluminum alloy to a phenolic laminate. The phenolic plastic expanded just about twice as much as the aluminum did. This difference was enough to cause the panels to fall off by themselves almost universally when heated and cooled over a significant temperature range. However, by judicious choice of the amounts of filler to be added to the phenolic, the expansion of the phenolic was reduced in half almost to match that of aluminum. The aluminum panel then adhered completely, and it could not be removed without tearing the metal or rupturing the phenolic core [1].

Propellants and explosives have physical characteristics very similar to those of plastics. Indeed some solid propellants are plastics themselves, such as polyurethanes, polyesters and other composite propellants. The coefficient of thermal expansion, hereafter referred to as the expansivity, of a given propellant could be as much as twenty times as great as that of its container. Consider a 30-foot long rocket chamber made of mild steel. Over a temperature range of only 25 °C (45 °F), the metal chamber would change only 0.1 inch in length whereas the propellant inside it would change more than 1.5 inches. If allowance were not made for this large difference in expansion or contraction, then most certainly large thermal strains would be caused within the propellant grain which could cause mechanical failure of the grain and a change in the geometrical configuration of the grain, either one

of which would affect the thrust of the rocket motor [2]. Of course many rocket motors are subjected to much greater temperature cycles than 45 °F in severe climates in a 24-hour period. It has been found [3] that in parked aircraft, temperatures well over 200 °F have been observed beneath the closed canopy at pilot head level. The propellant cartridge actuated devices (CAD) which are used to remove the canopy or eject the pilot are thus exposed to extreme temperature cycles themselves.

Powdered aluminum is sometimes added to certain propellants to increase the specific impulse. The expansivity of aluminum is generally much lower than that of the propellant. Thus the expansivity of the mixture of the two would be expected to lie somewhere between that of the individual components. The oxidizing agents as well as other additives would be expected to lower the expansivity of the composite mixture also.

The purpose of this author's investigation was to determine what effect an aluminum additive has on the expansivity of a composite plastic substance, the amount of the effect, and what correlation exists between the observed effect and the amount of aluminum that is added to the plastic.

Because of the lack of proper facilities to make and store actual propellants, and because of the inherent dangers in handling them, tests were run on plastic samples whose thermal properties closely approximated the properties of many actual composite propellants. An inert salt was added as a filler to the plastic resin to simulate the oxidizer component and amounts of aluminum

up to 20% by weight were added to different samples as the variable.

2. Theory

The linear coefficient of thermal expansion, also referred to as linear expansivity and designated by the letter "c", is the ratio of the change in length per degree to the length measured at the initial temperature. Thus c has the dimensions of inch/inch-degree or cm/cm-degree. The linear expansivity is small as shown here by a few examples [4]:

Material	c
glass and ceramics	0.1 to 1.0×10^{-5} cm/cm°C
steel	1.2
brass	1.9
aluminum	2.4
organic thermoset plastics	2-5
wood:	
parallel to grain	0.2-0.6
across the grain	2-6
organic thermoplastics	6-20

The final length (l_t) of a steel rod initially of the length (l_o) 10.0000 cm long and raised 10°C in temperature would be,

$$l_t = l_o\,(1 + c\,\Delta T)$$

$$l_t = (10)\left[1 + (1.2 \times 10^{-5})(10)\right]$$

$$= 10.0012 \text{ cm}$$

The cubical coefficient of thermal expansion, or cubic expansivity, a, is the ratio of the increase in volume per degree to the

original volume. For isotropic solid materials the cubic expansivity equals three times the linear expansivity.

$$a = 3c$$

In anisotropic solid materials this is not the case, for the material may expand different amounts in the three directions - length, breadth, and width. As shown in the table above for wood, as an example, the expansivity in width or breadth is 10 times the expansivity in length. An empirical equation for the cubic expansivity might be,

$$a = c \text{ (parallel)} + 2\, c \text{ (perpendicular)}.$$

Very little is known about the relation between expansivity and chemical composition [5]. Even less appears to be known about the relation between expansivity and physical composition in mixtures.

In the plastic cement field it has been shown [6] that for cements, the cubic expansivity, $a_{(mix)}$, is related to the coefficients of the individual components (a_1, a_2, . . .), the weight percent of each component (n_1, n_2, . . .) and a factor (b_1, b_2, . . .) which is a characteristic of each material:

$$a_{(mix)} = \frac{a_1\, n_1\, b_1 + a_2\, n_2\, b_2 + \cdots\cdots}{n_1\, b_1 + n_2\, b_2 + \cdots\cdots}$$

The factor "b" for a material is proportional to the product of its bulk compression modulus of elasticity, M_B, and its specific volume, v,

$$b \propto M_B\, v$$

or, since $v = \dfrac{1}{\rho} = \dfrac{1}{\text{density}}$,

$$b \propto \frac{M_B}{\rho} \quad \text{or} \quad b = \text{(proportionality constant)}\, \frac{M_b}{\rho}$$

The bulk modulus is known exactly for only a few materials; however, the factor b may be regarded as an empirical constant characteristic of each material. Thus in a two-component mixture, with the factor b_1 of one component known, the factor b_2 of the remaining component can be determined empirically. The empirically obtained b_2 and the known b_1 can then be used in calculations involving other mixtures.

The only explanation of why the factor b is based on the bulk compression modulus and the density of a component is an intuitive one. Apparently adjoining particles of different expansivities in a uniform mixture exert pressures on each other as they thermally expand. Since the particles of one component may be more easily compressed than particles of other components, they are not allowed to contribute as much to the overall expansivity of the mixture as they would if all components had the same compressibility.

3. Apparatus

Various methods of determining the expansivity of materials were considered, some of which are described elsewhere [5, 7, 8, 9, and 10]. A considerable amount of work was actually done by the author on the linear expansivity of several different propellants and explosives at the Naval Ordnance Test Station, China Lake, California during a six-week tour of duty there in June-July 1959. In the author's opinion, the apparatus used there [8] was more accurate and much more convenient to use than the apparatus described in ASTM: Test D 864-52 [9]. The results obtained were assigned a security

classification of CONFIDENTIAL. This apparatus for linear expansivity had several good features in that it directly recorded the experimental results in graphical form, thus reducing much of the tedious manual recording and adjustments otherwise necessary. In addition, it gave quite accurate results when the equipment was calibrated very carefully.

The apparatus which was used to obtain the results reported in this thesis was the same as that described by Briggs [10], with one modification. Figures 1 and 2 show the Dilatometer and its assembly. It was found that the Kern-Exelo stopcock could be tightened sufficiently to prevent the leakage of mercury out of the stopcock when it was immersed under the water bath level. Later during experimental runs, it was found that water did leak into the filling end of the stopcock, but of course this was of no consequence to the remainder of the assembly. Therefore, the lower section of the dilatometer was not so fragile and was much easier to handle in cleaning, assembly and operation.

An easy way to handle the apparatus was developed by means of movable arms and two-way (contort) swivel clamps. Figure 2 shows the apparatus down in the bath. The dilatometer was raised out of the bath by pushing the dilatometer supporting rod up with one hand and the retaining rod was clamped onto the lower arm with the other hand. It was an easy matter to pour the mercury out through the capillary when finished with a run by locking the dilatometer in the up-out-of-bath position described above, disconnecting the upper arm from the dilatometer supporting rod, and rotating the

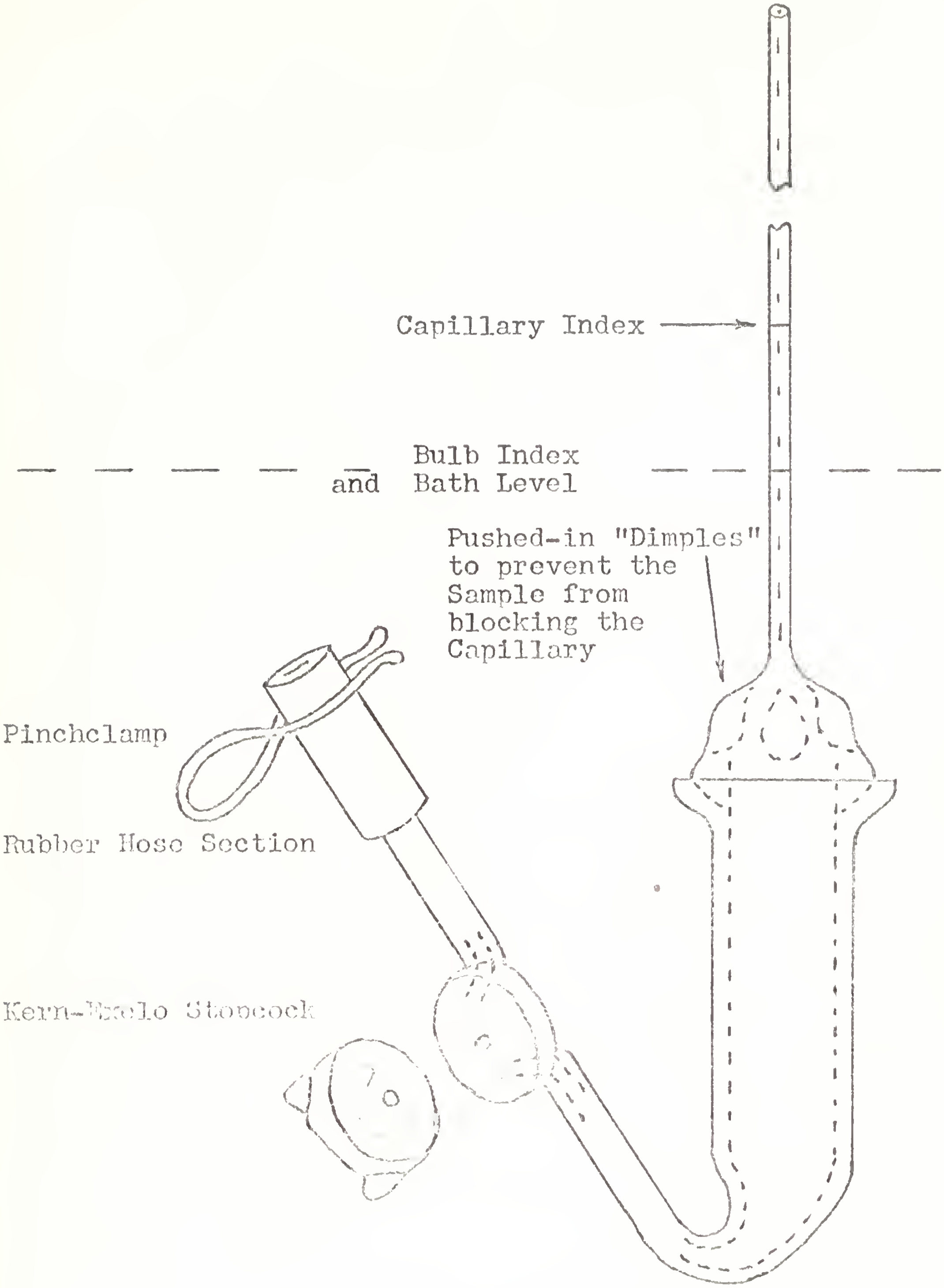

FIGURE 1. DILATOMETER

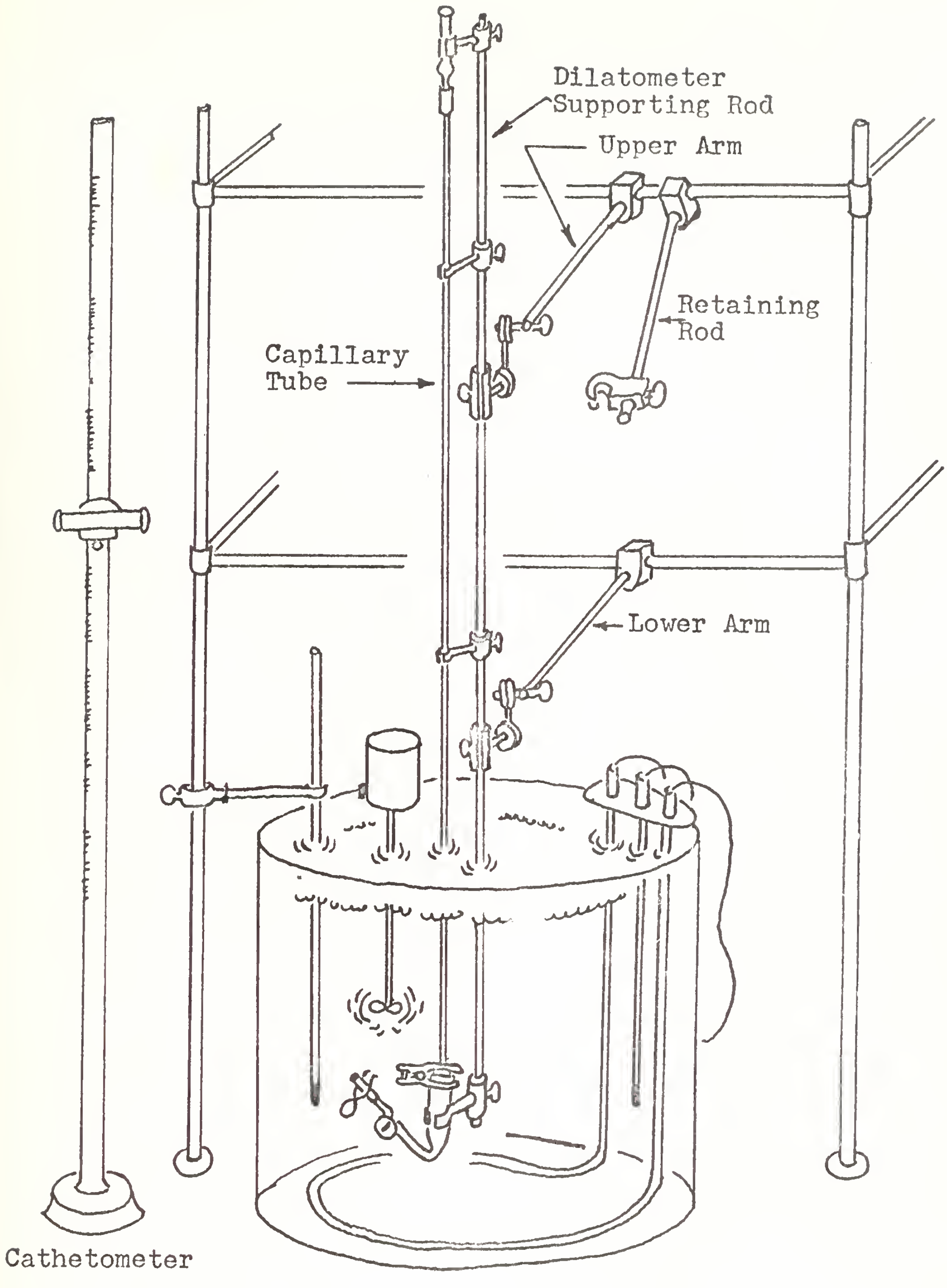

FIGURE 2. DILATOMETER ASSEMBLY

dilatometer supporting rod about 135 degrees to the right or left. The procedure for removing the mercury is described in greater detail in Appendix II. During all these manipulations, the fragile glass dilatometer was clamped firmly to the supporting rod thereby reducing the chances for breakage.

The two sections of the sample bulb which were joined by a spherical ball and socket ground glass joint, were clamped together with the metal c-clamp commonly used with this type of joint, and in addition enough DeKhotinsky cement was applied to the joint to insure a tight and immovable fit. The cement was easily applied by slightly warming the clamped joint with a bunsen burner flame, and then applying the warmed cement to the outside of the joint with a heated spatula. This was done in two steps by applying the cement to one-half of the joint, allowing it to cool and harden, then rotating the clamp 180° around the joint and applying cement to the remainder of the joint. The cement was easily removed by warming it with a flame, picking off the majority of the cement with a spatula. Further heating allowed the two sections to be pulled apart easily. The cement remaining on the two sections was then easily removed by scrubbing it with methanol.

Three parameters were determined for this apparatus: the volume of the sample bulb (V_o), the volume of the capillary from the capillary index to any point along its length (ΔV), and the effect of the volume of the glassware (V_g) and its cubic expansivity (a_g).

The volume of the bulb was determined by joining and sealing the two empty bulb sections, filling the system to the capillary

index with mercury, bringing it to a constant temperature, removing the mercury, weighing it on a trip-balance, and then dividing the weight by the density of mercury. This procedure was repeated until the bulb sections could always be assembled to give reproducible results.

The cross-sectional area of the capillary was found to be critical in regard to the final results. The cross-sectional area of the capillary tube was determined precisely by the method described by Briggs in his Appendix II [10] . It was found that the cross-sectional area of the capillary varied from a minimum value of 3.455×10^{-3} cm^2 at 30.675 cm from the index to a maximum value of 3.573×10^{-3} cm^2 at 54.970 cm from the index. (See Fig. 3). The volume of the capillary at any location from the capillary index was determined by integrating (using the trapezoidal rule) under the curve of cross-sectional area plotted versus distance from the capillary index. These data were tabulated for use during a run as described in Section 5 under Treatment of Data.

The effect of the volume of glassware (V_g) and its cubic expansivity (a_g) was determined empirically for the apparatus. The volume of glassware was assumed to be equal to that of the sample bulb, i.e. $V_g = V_o$ [13]. The linear expansivity of pyrex was found in the literature to be quoted as 3.25×10^{-0} /°C, but this value is dependent on the particular manufacturer and was found to change after fabrication as reported by Briggs [10]. In addition, the dimpled sections, joint and filling connection with the stopcock had some effect on the overall expansivity of the glass. Thus the

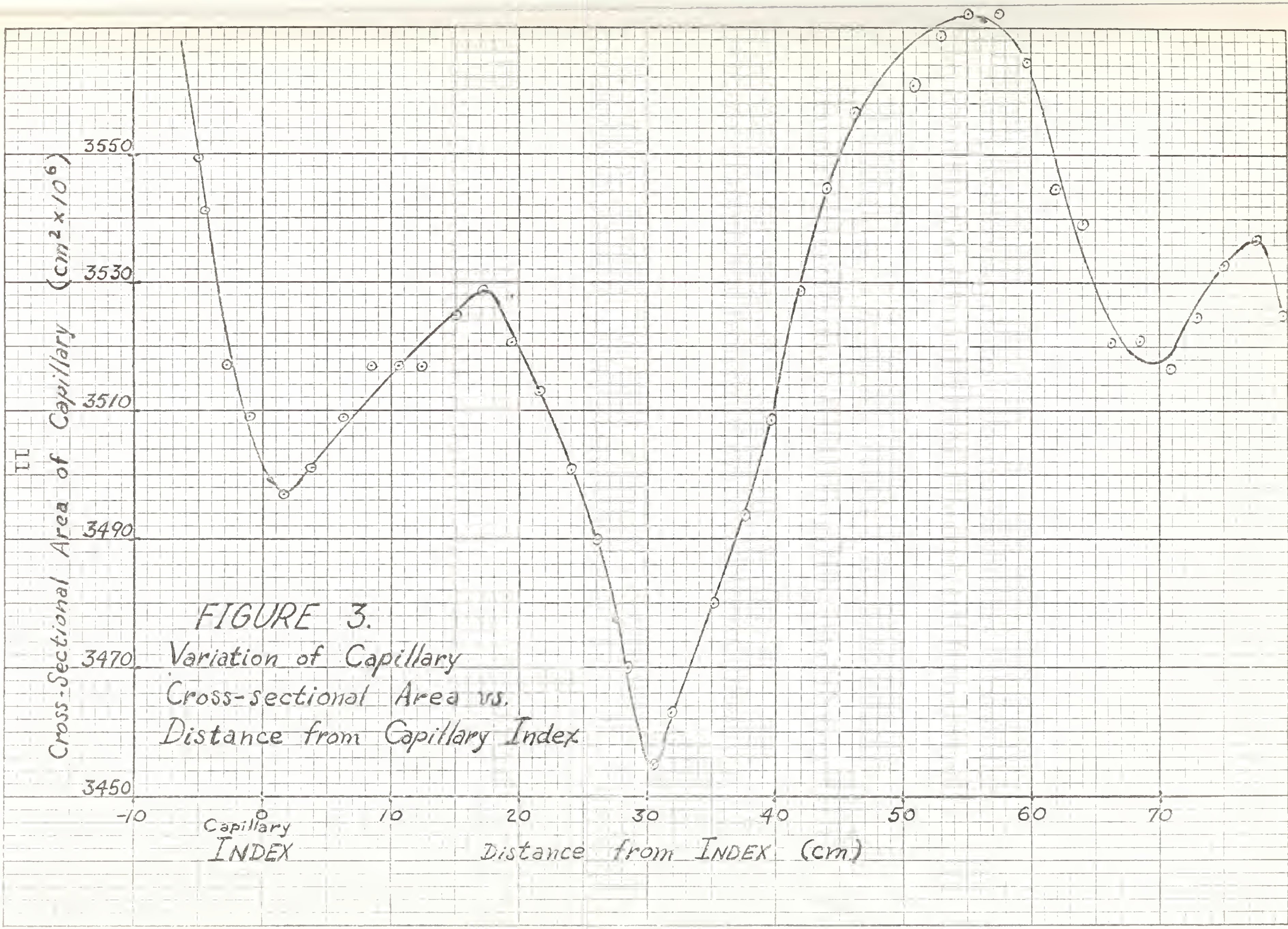

FIGURE 3.
Variation of Capillary Cross-sectional Area vs. Distance from Capillary Index

cubic expansivity could be assumed to be of the same magnitude as three times the linear expansivity, or about $1.0 \times 10^{-5}/^{\circ}C$. The actual value for the expansivity of the glassware was found to be $1.246 \times 10^{-5}/^{\circ}C$. This was determined by conducting a calibration operation using mercury alone in the system and the known cubic expansivity of mercury.

Although not an integral part of the apparatus, the thermometer used to determine the temperature and temperature changes in the bath had to be calibrated. Five Beckmann thermometers were calibrated over the temperature range 25°-50°C by comparing them with a thermometer which had been checked by the National Bureau of Standards. During the period of investigation it was found that the Beckmann thermometers were not as precise as originally believed, and cumulative errors as great as 0.1°C were detected over a 25°C temperature range. These errors were no doubt due to thermometer lag, stem corrections and/or temporary bulb volume changes. Consequently the standardized thermometer was used for all runs and the Beckmann thermometers were used as a good check on the constancy of the bath temperature. By using the cathetometer, the temperature could be determined correctly to 0.01 of a degree.

The temperature of the water bath was regulated by a Precision Micro-Set Differential Range Thermoregulator manufactured by the Precision Scientific Company. It was designed to have a sensitivity of ±0.005°F and it was found to control the bath temperature within 0.01°C very easily. About 2.2 collar turns were found to be equivalent to a change of 1°C.

Determination of the location of the capillary index, movement of the mercury meniscus and the temperature reading was accomplished with a precision cathetometer, accurate to ± 0.005 centimeters.

Operating instructions for using this apparatus are given in Appendix II.

4. Preparation of Sample

It was desired to have plastic samples that had expansivity characteristics similar to those of composite propellants, yet not be hazardous to handle. It was also desired that the expansivity of the plastic be relatively large so that the effects of additives would be readily apparent.

The resin had to be one that was fairly stable, easy to polymerize and cure, and castable. A mixed polyester resin was obtained through the courtesy of Mrs. Mary M. Williams, Code 5052, NOTS, China Lake, California. This resin consisted of 55% Vibrin 121 and 45% Selectron 5119 with a cobalt naphthenate accelerator added to it. This resin was stable at room temperature for about 30 days when new, but at 40°F was stable for six months to a year. In order to simulate the effect of a propellant oxidizer, an inert salt, K_2SO_4, was mixed with the resin. Finally, powdered aluminum was added in various amounts to different samples.

The samples were made by the very simple procedure of pouring the resin-additive mixture into six-inch test tubes. Then the plastic polymerized in the tubes upon the addition of the catalyst. The test tubes were selected so that their inner diameter was a

little less than that of the apparatus bulb section in order that the samples would have room for expansion during the run. The casting procedure which was used is described in Appendix I.

One resin-sulfate-aluminum sample was sectioned in several pieces and examined with a magnifying glass for evidences of entrapped air bubbles or pockets, but none were apparent. The sample appeared to be a uniform mixture throughout its length as well as across its diameter. Evidently the sample de-gassed itself in the polymerization process.

It was necessary to condition the samples in order to exclude (or at least minimize) changes of sample volume which might have been caused by changes in moisture content, post-curing, loss of plasticizer or solvents, release of stresses and other factors. The conditioning method which was used is described in Appendix I and was based on methods reported elsewhere [11].

5. Treatment of Data

The raw data which were recorded for every sample during a run were the location of the capillary index, the location of the mercury meniscus, and the exact temperature for every change in temperature. Before the data were recorded, the dilatometer, mercury and sample were allowed to remain at the temperature long enough for equilibrium to be reached. For a 1°C temperature change sometimes as little as 15 minutes was sufficient, however over an hour was sometimes required at temperatures near 50°C. Corresponding to every temperature increment was a capillary length increment, Δl. The net volume change, ΔV, (the expansion of the mercury,

glassware and sample) was found by entering the table made up for this purpose as described in Section 3. Tables 1 through 5 show the data which were obtained from runs conducted on five different samples. The composition of each sample is noted in weight percentages. In these tables, Δl is the distance (in centimeters) from the capillary index to the mercury meniscus in the capillary tube of the dilatometer at the corresponding temperature. ΔV is the volume (in cubic centimeters x 10^4) of the capillary occupied by the corresponding Δl. T is the temperature in degrees centigrade, $^{\circ}C$. As a run was in progress, ΔV vs. T was plotted and any irregularities were immediately detected. (See Fig. 4). No real conclusions could be drawn from the comparison of the curves shown in this figure because each sample had a different initial volume.

The calculation of the cubic expansivity was based on the following assumptions and calculations:

$$V_2 = V_1 + V_1 a (T_2 - T_1)$$

$$a = \frac{V_2 - V_1}{V_1 (T_2 - T_1)} = \frac{\Delta V}{V \Delta T}$$

In this dilatometer, the volume change was a combination of a rise of mercury in the capillary due to the expansion of mercury and the sample and a drop in the mercury level due to the expansion of the glass bulb and tubing. Consequently,

$$\Delta V = (a_m V_m + a_s V_s - a_g V_g) \Delta T$$

$$a_s V_s \Delta T = \Delta V + a_g V_g \Delta T - a_m V_m \Delta T$$

$$a_s = \frac{\Delta V}{V_s \Delta T} - a_m \frac{V_m}{V_s} + a_g \frac{V_g}{V_s}$$

Table I

Sample composition: 100% resin, 0% K_2SO_4, 0% aluminum

weight: 14.0226 gms

volume: 11.71 cm^3

density: 1.197 gms/cm^3

Δ l	Δ V	T
0.0	0.0	25.0
2.160	75.572	26.0
4.335	151.678	27.0
6.500	227.642	28.0
8.675	304.105	29.0
21.400	752.129	35.0
23.680	832.108	36.0
25.975	912.355	37.0
28.290	992.927	38.0
44.640	1564.007	45.0
47.045	1649.520	46.0
49.360	1732.003	47.0

Table 2

Sample composition: 50% resin, 50% K_2SO_4, 0% aluminum

weight: 21.2352 gms

volume: 13.03 cm^3

density: 1.630 gms/cm^3

Δ l	Δ V	T
0.0	0.0	25.0
1.610	56.335	26.0
3.260	114.053	27.0
19.200	674.750	36.0
21.000	738.079	37.0
22.800	801.270	38.0
39.340	1376.978	47.0
41.140	1440.242	48.0
42.965	1504.650	49.0

Table 3

Sample composition: 45.0% resin, 45.0% K_2SO_4, 10.0% aluminum

weight: 20.6019 gms

volume: 12.16 cm^3

density: 1.694 gms/cm^3

Δl	ΔV	T
0.0	0.0	25.0
1.535	53.712	26.0
3.120	139.953	27.0
4.690	164.129	28.0
6.300	220.616	29.0
16.075	564.557	35.0
17.670	620.827	36.0
19.325	679.150	37.0
20.985	737.552	38.0
32.865	1151.244	45.0
34.610	1211.801	46.0
38.115	1334.054	48.0
39.605	1386.277	49.0
41.295	1445.706	50.0

Table 4

Sample composition: 44.45% resin, 44.45% K_2SO_4, 11.1% aluminum

weight: 21.7261 gms

volume: 12.82 cm^3

density: 1.695 gms/cm^3

Δ 1	Δ V	T
0.0	0.0	25.0
1.495	52.313	26.0
3.045	106.528	27.0
17.755	623.826	36.0
19.380	681.087	37.0
20.990	737.727	38.0
36.705	1284.778	47.0
38.230	1338.082	48.0
39.980	1399.436	49.0

Table 5

Sample composition: 40.0% resin, 40.0% K_2SO_4, 20.0% aluminum

weight: 21.6066 gms

volume: 12.38 cm^3

density: 1.745 gms/cm^3

Δ l	Δ V	T
0.0	0.0	25.0
1.390	48.640	26.0
2.795	97.783	27.0
4.280	149.764	28.0
5.695	199.376	29.0
14.825	520.483	35.0
16.400	576.024	36.0
17.920	629.646	37.0
19.465	684.079	38.0
32.275	1130.819	46.0
33.895	1186.961	47.0
35.485	1242.243	48.0
37.120	1299.267	49.0

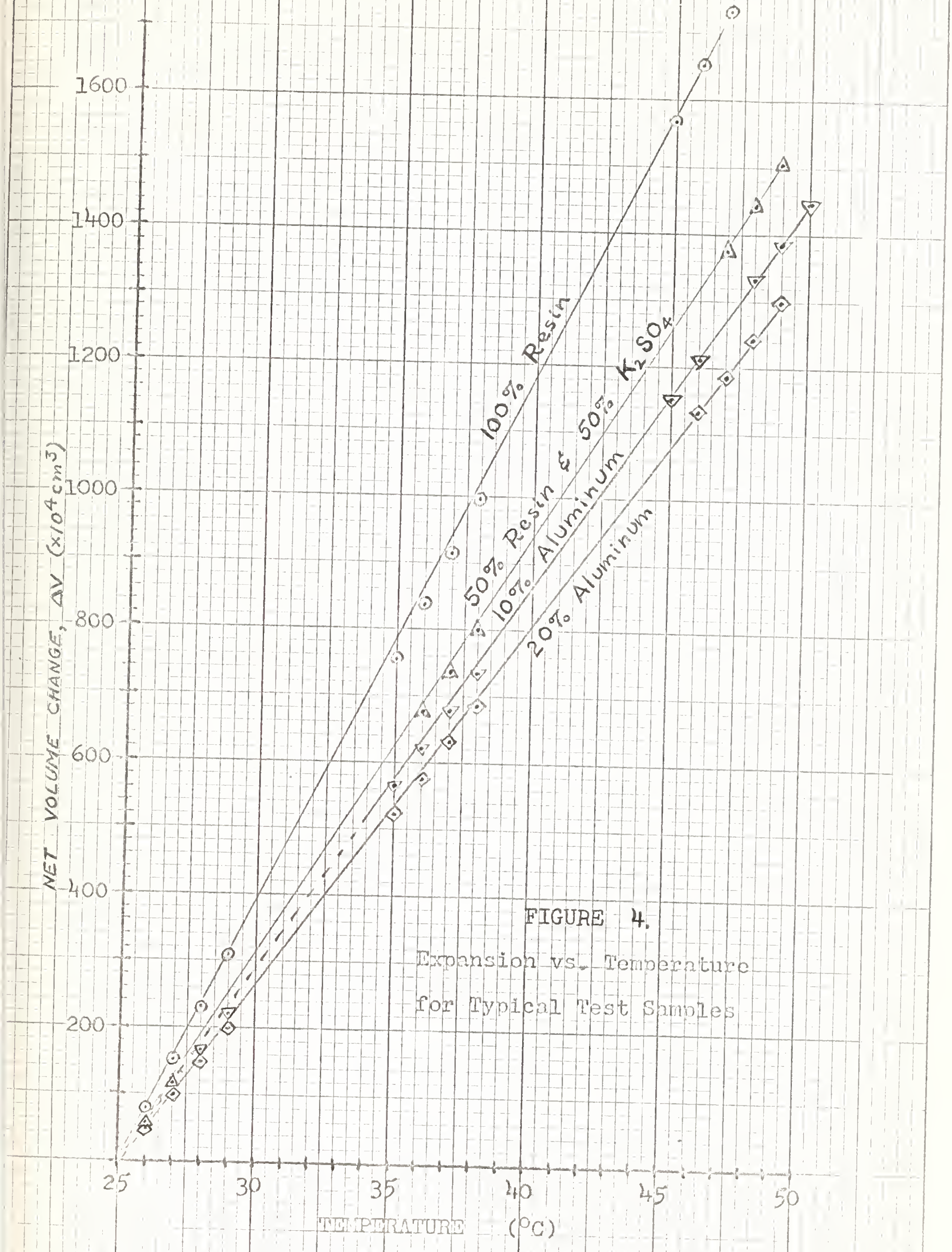

FIGURE 4.

Expansion vs. Temperature for Typical Test Samples

Substituting $V_o = V_m + V_s$

And assuming $V_g = V_o$ [12]

Then

$$a_s = \frac{\Delta V}{V_s \Delta T} - a_m \frac{V_o - V_s}{V_s} + a_g \frac{V_o}{V_s}$$

$$a_s = \frac{\Delta V}{V_s \Delta T} - \frac{V_o}{V_s}(a_m - a_g) + a_m$$

The values for V_o and a_g were constants for all experimental runs and were empirically determined for this apparatus to be:

$$V_o = 20.08 \ cm^3$$
$$a_g = 1.246 \times 10^{-5} \ cm^3/cm^3\text{-}^\circ C$$

The expansivity of mercury is [12]

$$a_m = 18.194 \times 10^{-5} \ cm^3/cm^3\text{-}^\circ C$$

Substituting these constants in the equation for a_s,

$$a_{s\,(observed)} = \frac{\Delta V}{V_s \Delta T} - \frac{20.08}{V_s}(18.194 - 1.246) \times 10^{-5} + 18.194 \times 10^{-5}$$

$$a_{s\,(obs)} = \frac{\Delta V}{V_s \Delta T} - \left(\frac{340.3}{V_s} - 18.194\right) \times 10^{-5}$$

The values for ΔV and ΔT were obtained from the data recorded during the run. The value for V_s was obtained in the manner described in the step-by-step operating procedure given in Appendix II.

6. Results

Data were obtained on five samples of different composition. The cubic expansivity was calculated with the greatest possible precision in order to be able to reach some valid conclusions when comparing the results of the individual tests to determine the effect of varying the amount of aluminum in each sample.

All samples were made of the same mixed resin, and all of the composite plastics contained equal parts (by weight) of resin and inert salt (K_2SO_4). The percentages given for the samples containing aluminum are weight % of aluminum, and the remainder of the samples are resin and salt. The observed values (except for 100% aluminum) were:

Cubic expansivity/°C

100% Resin	a_r	$= 56.36 \times 10^{-5}$
Resin and salt	a_{rs}	$= 40.19 \times 10^{-5}$
10.0% Aluminum	$a_{10.0\%}$	$= 37.77 \times 10^{-5}$
11.1% Aluminum	$a_{11.1\%}$	$= 37.13 \times 10^{-5}$
20.0% Aluminum	$a_{20.0\%}$	$= 34.44 \times 10^{-5}$
100% Aluminum [5]	a_{Al}	$= 6.825 \times 10^{-5}$

The first method used to determine the effect of aluminum additives was by the equation

$$a_{(mix)} = \frac{a_1 \, n_1 \, b_1 + a_2 \, n_2 \, b_2}{n_1 \, b_1 + n_2 \, b_2}$$

Neither the bulk compression modulus of elasticity, M_B, of the resin or of the resin-salt mixture was known, nor could they be determined

conveniently. It has been reported [5] that

$$K = \frac{3(1-2\mu)}{E}$$

where K = compressibility = $\frac{1}{M_B}$

μ = Poisson's ratio

E = Young's Modulus of Elasticity

and that at room temperature,

$$E_{Al} = 7.19 \times 10^5 \text{ kg/cm}^2 \quad \text{with } \mu = 0.33 \text{ and}$$

$$\rho_{Al} = 2.686 \text{ gms/cm}^3 .$$

Then by b = (proportionality constant) $\frac{M_b}{\rho}$, and assuming that the proportionality constant is equal to one,

$$b_{Al} = \frac{1}{K\rho} = \frac{E}{3(1-2\mu)\rho} = \frac{7.19 \times 10^5 \text{ kg/cm}^2}{2.686 \text{ gms/cm}^3} = 2.663 \times 10^8 \text{ gmf-cm/gmm}$$

The equation for $a_{(mix)}$ was solved to determine empirically the factor b_{rs} for the resin and salt mixture (treated together as one component) using the observed value of $a_{(mix)}$ for the 11.1% aluminum sample:

$$b_{rs} = \frac{m_{Al}\, b_{Al}\,(a_{Al} - a_{(mix)})}{m_{rs}\,(a_{(mix)} - a_{rs})} = 3.291 \times 10^8 \text{ gmf-cm/gmm}$$

(This value for b_{rs} would indicate that E_{rs} would have to equal about 7.6×10^6 psi. This is about the same magnitude of values reported for some similar mineral-filled plastics.) Using this empirical value obtained for b_{rs}, the predicted values of the cubic expansivity for the 10.0% and 20.0% aluminum samples were calculated to be:

$a_{10.0\%\ Al(calc)} = 37.4 \times 10^{-5}/^{o}C$

$a_{10.0\%\ Al(obs)} = 37.8 \times 10^{-5}/^{o}C$

$a_{20.0\%\ Al(calc)} = 34.6 \times 10^{-5}/^{o}C$

$a_{20.0\%\ Al(obs)} = 34.4 \times 10^{-5}/^{o}C$

The cubic expansivity was also calculated on the basis of three other hypotheses:

a. on a weight % basis:

$$a_{(mix)} = a_1 n_1 + a_2 n_2$$

where n_1 = weight % of resin plus salt

n_2 = weight % of aluminum

b. on a volume % basis:

$$a_{(mix)} = a_1 V_1 + a_2 V_2$$

where V_1 = volume % of resin plus salt

V_2 = volume % of aluminum

$$V_2 = (m_2) \frac{\text{(density of sample)}}{\text{(density of aluminum)}}$$

c. on an average of the values calculated on the weight % basis and the volume % basis:

$$a_{(mix)} = \frac{a_1(m_1 + V_1) + a_2(m_2 + V_2)}{2}$$

The values for $a(\times 10^{5}/^{o}C)$ obtained by these hypotheses are compared with the actual observed values and the values calculated using the factor b method:

	Samples containing weight % aluminum		
	10.0%	11.1%	20.0%
Calculations based on			
Weight % basis	36.9	36.5	33.5
Volume % basis	38.1	37.9	35.9
(Weight % + Volume %)/2	37.5	37.2	34.7
Observed value	37.8	37.1	34.4
Factor "b" basis	37.4		34.6

7. Discussion of Results

The results were determined from data on only one run on each sample. Consequently the validity of any conclusions drawn from these results would depend on the reproducibility of results which would be obtained with the apparatus and upon the variations to be expected between individual samples of the same composition and past history.

Despite the small number of samples used, it was found that aluminum additives, even in small amounts, lower the expansivity of a composite plastic by a significant degree. It was also found that the expansivity of the composite mixture can be predicted with an error of about 1% by the correlation

$$a_{(mix)} = \frac{a_1 n_1 b_1 + a_2 n_2 b_2 + \dots\dots}{n_1 b_1 + n_2 b_2 + \dots\dots}$$

where the factor b is proportional to the product of the bulk compression modulus of a component and its specific volume, and n is the weight percent of the component.

It was also found that predictions based on the relationship

$$a_{(mix)} = a_1 n_1 + a_2 n_2$$

gave consistently low results, and that predictions based on the relationship

$$a_{(mix)} = a_1 V_1 + a_2 V_2$$

where V is the volume percent of the individual component, gave consistently high results.

Furthermore it was found that predictions based on the relationship

$$a_{(mix)} = \frac{a_1 (n_1 + V_1) + a_2 (n_2 + V_2)}{2}$$

agreed almost exactly with predictions based on the method using factor b. No justification for this observation has been found in theoretical analysis.

It is believed by the author that the two correlations which were found to give fairly accurate predicted expansivities of mixtures may open a new approach to the consideration of additives to plastics and composite propellants. More research is definitely indicated in this field with the same mixtures to obtain a measure of the reproducibility of results as well as with mixtures of a larger number of components.

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APPENDIX I

CASTING AND CONDITIONING PROCEDURE

The step-by-step procedure which was found to be most satisfactory for casting and conditioning the samples is as follows:

1. Heat a sufficient quantity of K_2SO_4 and aluminum powder at 100°C for about 24 hours to remove moisture.

2. Clean and dry all test tubes, beakers and stirring rods thoroughly. Label each beaker and test tube to show what they are to contain.

3. Pour out enough resin in a large beaker to make the samples and return the remainder immediately to cold storage. Allow as little moisture as possible to condense inside the cold container.

4. Weigh the desired amounts of K_2SO_4 and aluminum powder into the individual beakers, grind them together with the glass stirring rod to remove all lumps, and thoroughly mix them to give as uniform a mixture as possible.

5. With the beaker containing the K_2SO_4 and aluminum powder on the trip balance, slowly add the desired amount of resin with stirring until the correct weight of resin has been added. Insure that all of the powder and aluminum is wetted by the resin.

6. As soon as all the different samples are thoroughly mixed, the casting procedure is completed on an individual basis. About 30 drops of methyl ethyl ketone peroxide catalyst are added to the resin-sulfate-aluminum mixture in the beaker and thoroughly stirred.

As soon as the mixture becomes noticeably viscous (after about five minutes) it is poured into the six-inch test tube. The resin then gells solid within a few minutes.

7. Treat each remaining mixture in turn as stated above.

8. Allow the samples to cure in their test tubes at room temperature for about 15 hours.

9. Remove the samples from the test tubes by gently tapping the inverted test tubes and let the sample slide out, or crack the glass gently and remove the broken glass carefully so as not to scratch or break the sample.

10. Mark or label the samples in some manner and allow them to remain in an oven at 50°C to cure for approximately one week.

11. Remove the samples from the oven, cut them (on a bandsaw) to the desired length to just fit inside the bulb sections of the apparatus, scrub them quickly with soapy water and rinse them with distilled water. Wipe the samples dry with lintless Kim-Wipes and put them into a 100°C oven for one-half hour, and then leave them in a 50°C oven for at least another week as a final curing and conditioning period.

12. At the end of the conditioning period place the samples in a dessicator until needed for a test.

APPENDIX II

OPERATING INSTRUCTIONS

The method of obtaining the cubic expansivity by dilatometric technique was not a fast one. Hours of preparation (sometimes days in advance) had to be done before commencing a run. For the runs covering the temperature range of 25°-50°C, as little as six hours or as much as 14 hours were required, depending on how accurately the temperature was controlled and how quickly the system reached equilibrium at the various temperatures.

Cleanliness of the apparatus, cleanliness of the mercury and samples, proper conditioning of the samples, and tight-fitting joints and stopcock were found to be major items affecting the accuracy and reproducibility of the results obtained.

The glassware was cleaned very carefully by washing it with sulfuric acid-sodium dichromate cleaning solution, rinsing it with tap water followed by several rinsings with distilled water, and drying it. The long capillary section was dried after the final rinse by inverting the tube in an upright position and applying a strong vacuum to the capillary end. By the procedure of draining and evaporation the tube was left clean and dry in about one hour. The short bulb section was easily dried after the final rinsing by placing it in an oven at about 100°C for a short time. After drying, the glassware was closed off from the atmosphere when not in use.

The cleanliness of the mercury was assured as much as possible by using triply-distilled mercury and filtering it through filter

paper with a pin-hole in it just prior to filling the dilatometer. The separatory funnel which contained the mercury and the short section of rubber tubing which joined the separation funnel to the dilatometer were cleaned carefully also. The samples were cleaned after they had cured at 50°C for one week by scrubbing them quickly with soapy water, drying immediately in an oven, curing again at 50°C for at least one more week, then storing in a dessicator when not in use. The samples were handled with lint-free tissue paper after the final curing.

The method which was used to condition the samples and the procedure for obtaining a tight-fitting joint is described in Sections 3 and 4 and Appendix I.

In general, the step-by-step procedure which was found to give the most satisfactory results is as follows:

1. Clean and dry the glassware, mercury and sample.

2. Clamp the lower bulb section in position above the water bath of the apparatus.

3. Insert the sample in the bulb. Fit the upper bulb section with the capillary tube to the lower bulb section and clamp in position on the apparatus.

4. Close the Kern-Excelo stopcock. Apply vacuum at the upper end of the capillary tube.

5. Clamp the joint together and seal with De Khotinsky cement.

6. Attach the mercury reservoir to the filling connection and apply vacuum to the dilatometer up to the reservoir stopcock.

7. Fill the dilatometer with mercury to a position 30 to 40 cm above the capillary index. Gentle tapping of the bulb as the mercury is poured in insures no trapping of air bubbles around the sample or joint.

8. Secure the vacuum and remove the vacuum hose from the top end of the capillary. Replace it with a drying tube.

9. Close the Kern-Excelo stopcock and then close the mercury reservoir stopcock leaving some mercury still in the filling connection. Then remove the mercury reservoir from the rubber connection and place aside.

10. Close the end of the short rubber hose on the filling connection with a pinch-clamp and manipulate the Kern-Excelo stopcock to allow the mercury in the capillary to fall to a position between the bulb index and the capillary index.

11. Immerse the dilatometer in the water bath (at 25°C) to the bulb index, and allow the mercury to seek its own level.

12. Observe the mercury meniscus with the cathetometer until there is no appreciable movement in a period of ten minutes. This means that the whole system, glass, mercury and sample, nearly reaches equilibrium at 25°C.

13. Adjust the mercury level so that it is fairly close to the capillary index by compressing the short rubber hose and manipulating the Kern-Excelo stopcock.

14. Repeat steps (12) and (13) as necessary until the entire system reaches equilibrium with the mercury meniscus located near the capillary index. This condition is met when the meniscus does

not move more than 0.005 cm in a period of 15 minutes. It requires from one to two hours to accomplish steps (12) through (14).

15. Record the position of the capillary index and the mercury meniscus at 25°C and at convenient intervals up to 50°C as the temperature control is adjusted. By recording the capillary index location each time the meniscus level is recorded, no readings are invalidated if the dilatometer is subsequently moved or jarred through accident or design during the progress of a run. It requires about 20 minutes per 1°C temperature change for the system to come to equilibrium.

16. Upon completion of the run, raise the dilatometer out of the water bath and remove the excess mercury which has been left in the filling connection with a suction device.

17. Detach one of the movable arms of the assembly from the dilatometer and rotate the dilatometer on the remaining 2-way swivel arm until the capillary end is about 30° below horizontal.

18. Place a small side-arm filter suction flask with a one-hole stopper over the end of the capillary. Open the Kern-Excelo stopcock and apply suction to the suction flask. The mercury is thus drained from the bulb and capillary into the suction flask. By tapping the dilatometer gently during this procedure all, or nearly all, of the mercury is removed from it.

19. Remove the suction flask containing the mercury and rotate the dilatometer to an upright position and fix in place. Warm the De Khotinsky cement slightly and scrape the cement off the joint. The joint is then easily broken.

20. Remove the sample from the bulb and weigh it in order to determine its density later.

21. Add any mercury left in the bulb to the mercury in the filter suction flask. Obtain the weight of the mercury by subtracting the weight of the bottle from the weight of the bottle and mercury. Obtain the volume of mercury, V_m, by dividing the weight by the density of mercury at 25°C.

22. Obtain the bulb volume, V_o, from previous calibration data corrected for the mercury meniscus location with respect to the bulb index or capillary index. (For this apparatus, $V_o = 20.08$ cm^3, the bulb index is 4.520 cm below the capillary index, and the volume of the capillary from the bulb index to the capillary is 0.0159 cm^3. Thus, as long as the mercury meniscus is located at 25°C somewhere between the bulb index and the capillary index, the volume can be assumed to be 20.1 cm^3 with only about 0.2% error.)

23. Determine the sample volume, V_s, by subtracting V_m from V_o , and obtain the density of the sample by dividing V_s by the weight of the sample.